Ionic Liquid Mediated Sol-Gel Synthesis of Porous Silica

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This is to certify that the dissertation entitled **"IONIC LIQUID MEDIATED SOL-GEL SYNTHESIS OF POROUS SILICA"** *being submitted by* ***AUROBINDA MOHANTY*** *to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by them under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.*

Rourkela-769 008 ***Dr. Priyabrat Dash***
Date Supervisor

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AurobindaMohanty

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INTRODUCTION

1.1.General Introduction on Porous Silica

Porous material is a material containing pores. The skeletal portion of the material is often called the "matrix" or "frame". The pores are typically filled with a fluid (liquid or gas). The skeletal material is usually a solid, but structures like foams are often also usefully analyzed using concept of porous media[1].A porous medium is most often characterized by its porosity. Other properties of the medium (e.g., permeability, tensile strength, electrical conductivity) can sometimes be derived from the respective properties of its constituents (solid matrix and fluid) and the media porosity and pores structure [2].Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure [3]. The size of the pores is generally 100 nanometers or smaller. Most Nano porous materials can be classified as bulk materials or membranes. Activated carbon and zeolites are two examples of bulk nanoporous materials, while cell membranes can be thought of as nanoporous membranes. Nanoporous materials abound in nature, both in biological systems and in natural minerals [4].

Porous silica is a form of the chemical element silicon that has introduced nanoporous holes in its microstructure. Porous silica are several types like silica nanoparticle, silica ionogels.

Silica nanoparticles are inorganic particles made of saline-based precursors, able to conjugated with functional groups of dyes and drugs. Typically, they are ultrafine particles(less than 100 nm), presenting approved safety, high bio stability and good bio distribution. Therefore, it can be applied for various biomedical applications, especially in cancer, such as fluorescent imaging, drug delivery, biosensors, and biomarkers. Among them, fluorescent silica nanoparticles have recently attracted intensive interest in cancer.

1.2 Silica Ionogels

Silica ionogels are the subject of a growing number of both fundamental and applied studies in materials science. They are a new type of material which consists of an ionic liquid confined within the backbone of a gel-like structure [5]. Ionic Liquid can be described as organic salts combining many favourable physicochemical properties including low melting points, negligible vapour pressure, high ionic conductivities and thermal stability [6]. This

has made Ionic Liquid interesting candidates for a number of applications including electrolytes for solar-cells, fluorescent and optical devices [7].So far, two routes have been highlighted for the incorporation of ILs in a gel; the organic route, which involves in situ polymerization or swelling of polymers with ionic liquid and the inorganic route, which consists of impregnation of ionic liquid within oxide backbones [8]. Of the inorganic routes, the polymeric sol-gel process is probably the most popular synthetic route. It involves hydrolysis and condensation reactions of inorganic or hybrid precursors in order to develop inorganic backbones with morphologies ranging from macro porous materials to dense bulk materials [9] depending on the hydrolysis conditions. The incorporation of ILs within sol-gel materials has been reported mainly on silicate based materials [10], where confinement and dynamics of ionic liquid within mesoporous structures has been demonstrated. However, one major disadvantage of these materials is their limited mechanical resistance due to the low connectivity of the inorganic network, because of the low drying temperatures and the characteristic liquid property of the ionic liquid [11]. An interesting approach to improve on the existing conductivity properties of solid- state electrolytes consists of the addition of co-encapsulants that exhibit electronic conductivity [12].

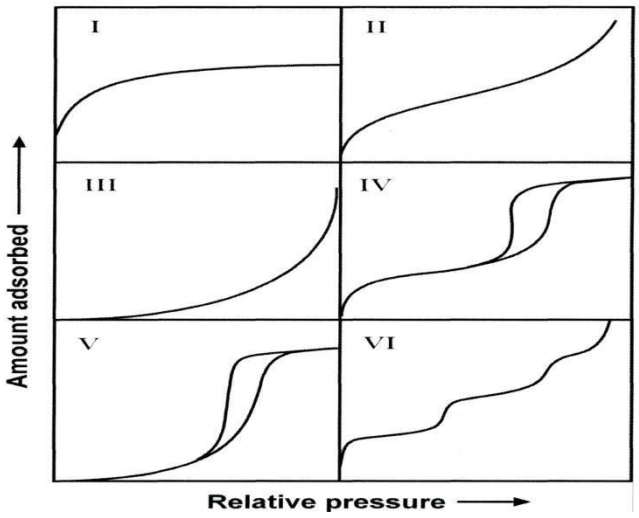
1.3 Mesoporous Silica Nanoparticles

Porous materials have become more and more important in either science or technology. They can be grouped into three classes based on their pore diameter (d): microporous, $d < 2.0$ nm; mesoporous, $2.0 < d < 50$ nm; macroporous, $d > 50$ nm. Among them, mesoporous materials have attracted more attention due to tailoring ability of the pore structure over a wide range, and the potential applications in catalysis [13]. Mesoporous silica is a form of silica and a recent development in nanotechnology [14]. Mesoporous materials with well-defined pore geometry have attracted considerable attention due to their high surface area, pore volume, and uniform pore channel for use in a wide range of application areas such as catalysts, molecular recognition as in a chemical sensor, and separation processes [15]. Among the wide variety of potential application areas, in particular, the development of functionalized mesoporous silica for liquid-phase separation application has attracted a great deal of interest, due to easy-tunable surface functionality and uniform pore structure [16]. In general, separation performances such as selectivity for the target and permeability through a membrane are strongly dependent on the surface functionality of membranes, its pore size and distribution, and the pore volume fraction [17]. Therefore, ordered mesoporous silica featuring a uniform, monodispersed pore size, high surface area, pore volume, and the easy

introduction of a surface functionality represents a promising separation layer for producing a high-performance membrane [18]. Functionalization of the surface of these mesoporous materials with organic or inorganic functional group leads to new physical and chemical properties [19]. These modified materials can be used in variety of applications such as catalysis adsorption and separation as chromatographic column packing. Porous materials created by nature or by synthetic design have found great utility in all aspects of human activities. Their pore structure is usually formed in the stages of crystallization or by subsequent treatment and consists of isolated or interconnected pores that may have similar or different shapes and sizes. Porous materials with small pore diameters (0.3 nm to 10 μm) are being studied for their molecular sieving properties [20]. The pore shape can be roughly approximated by any of the following three basic pore models, (a) cylindrical (b) ink-bottled and (c) slit-shaped pores. Depending on the predominant pore sizes, the porous solid materials are classified by IUPAC: Micro porous materials, (1) having pore diameters up to 2.0 nm; (2) having pore sizes intermediate between 2.0 and 50.0 nm; and (3) macroporous materials, having pore sizes exceeding 50 nm [21].

The pore size is generally specified as the pore width which is defined as the distance between the two opposite walls. Obviously, pore size has a precise meaning only when the geometrical shape is well defined. Porosity of a material is usually defined as the ratio of the volume of pores and voids to the volume occupied by the solid. Porous materials are also defined in terms of their adsorption properties [22]. The term adsorption originally denoted the condensation of gas on a free surface as opposed to its entry into the bulk, as in absorption. Adsorption of a gas by a porous material is described quantitatively by an adsorption isotherm, the amount of gas adsorbed by the material at a fixed temperature as a function of pressure [23]. Porous materials are most frequently characterized in terms of pore sizes derived from gas sorption data, and IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption [24].

The classification of adsorption isotherm are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III, and VI), or mesoporous (types IV and V)[25].The IUPAC classification of adsorption isotherms showing both the adsorptionand desorption pathways. Note the hysteresis in types IV and V.



The adsorption hysteresis in Figure (IV and V) is classified and it is widely accepted that there is a correlation between the shape of the hysteresis loop and the texture (e.g., pore size distribution, pore geometry, and connectivity) of a mesoporous material [26].

1.4 Sol-Gel Science Involved in the Synthesis of Porous Materials

The sol-gel process involves transformation of a sol to a gel. A sol is defined as a colloid of small particles that are dispersed into a liquid. A gel on the other hand is a rigid non-fluid mass and is usually a substance made up of a continuous network including a continuous liquid phase [27]. Therefore, sol-gel reactions involve hydrolysis and condensation reactions of inorganic alkoxide monomers in order to develop colloidal particles (sol) and consequently convert them into a network (gel) [28]. A metal or metalloid element bound to various reactive ligands represents the precursor used to synthesize the colloids. Metal alkoxides are the reagents most used for this purpose due to their ease of hydrolysis in the presence of water. Alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), are extensively used for the production of silica gels [29].Organic/inorganic hybrid materials prepared by the sol-gel approach have rapidly become a fascinating new field of research in materials science [30]. The explosion of activity in this area in the past two decades has resulted in tremendous progress in both the fundamental understanding of the sol-gel process

and the development and applications of new organic/inorganic hybrid materials[31]. Sol-gel reactions are those which convert an aqueous metal alkoxide solution into an inorganic network. The sol-gel method is also capable of producing homogeneous, high purity inorganic oxide glasses at room temperature, much lower than the high temperatures required by the conventional glass manufacturing process. For example, silica can be obtained from melt processing glass, but the sol-gel method is more effective for the production of amorphous silica. Another advantage of the sol-gel procedure is its ability to produce silica in different forms such as molded gels, spun fibers, thin films, molecular cages, aerogels, xerogels, and mesoporous materials for a variety of applications such as gas, and liquid separations, optical coatings, protective films, membranes, and catalysis [32]. Therefore, changing the conditions of sol-gel polymerization and processing is helpful for controlling the bulk properties of silica. Among the advantages of using the sol-gel method is the availability of its raw materials in high purity [33]. Modification of diverse properties of the inorganic network resulting from the sol-gel reaction is possible through the incorporation of the inorganic compound into different organic polymers.

1.5 Ionic liquid as a novel media for the synthesis of porous silica

The definition of ionic liquids allows distinguishing them from a classical molten salt. Amolten salt is mostly a high-melting, highly viscous and very corrosive substance while ionic liquids are already liquid at lower temperatures (< 100°C) and exhibit in most cases relatively low viscosities [34]. ILs typically contains bulky organic cations with a low degree of symmetry such as imidazolium, pyrrolidinium, tetraalkylphosphonium, trialkylsulfonium or quaternary ammonium [35]. Ionic liquids (ILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses [36]. The terms room temperature ionic liquid (RTIL), non-aqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase [37]. ILs is known as salts that are liquid at room temperature in contrast to high-temperature molten salts [38].

ILs has been known for a long time, but their extensive useas solvents in chemical processes for synthesis and catalysis has recently become significant. ILs became one of the most promising chemicals as solvents. Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them with volatile organic solvents, making new materials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting a variety of catalysts, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions[39].

. ILs have a wide liquidsranges [41]. The adopted upper melting temperature limit for the classification as 'IL' is known as 100 ^{o}C and higher melting ion systems are generally referred as molten salts. ILs remains liquid at room temperaturedue to the reason that their ions do not pack well. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase [42].The low melting points of ILs are a result of the chemical composition.The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point .ILs posses several advantages over conventional organic solvents, which make them environmentally compatible.

• ILs is highly polar.

• ILs consists of loosely coordinating bulky ions.

• ILs does not evaporate since they have very low vapour pressures.

• ILs is thermally stable, approximately up to 300° C.

• Most of ILs has a liquid window of up to 200° C which enables wide kinetic control.

• ILs has high thermal conductivity and a large electrochemical window.

• ILs is immiscible with many organic solvents.

• ILs is non aqueous polar alternatives for phase transfer processes.

• The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations.

Generally, the above statements are valid for the most commonly used ILs. However, one should note that there are many ILs containing different anions and cations and their

properties cover a vast range. Therefore, the above statements should not be generalized for all existing ILs and for those designed in the future. The acidic ionic liquids can act both as catalyst and as solvent. In this work, efforts were carried out to synthesize and use acidic ionic liquids for the synthesis of silica ionogel and subsequent removal of ionic liquid for the formation of porous silica. Also, the use of a new type of OMIMCl ionic liquid for the synthesis of silica nanoparticles has been explored.

1.6 Objectives of the present study

1. Synthesis, purification and characterization of different ionic liquids such as BMIMCl,OMIMCl, and $OMIMHSO_4$.
2. Synthesis of silica ionogels using Sol-gel method involving either neutral water or formic acid as a reactant.
4. To determine the best conditions to confine a maximum of ionic liquid (IL) inside silica-based matrixes and to reach the highest porosity after removing the IL from the ion gels.
5. To characterization of silica ionogel and silica nanoparticles by TGA and SEM.

Chapter-2

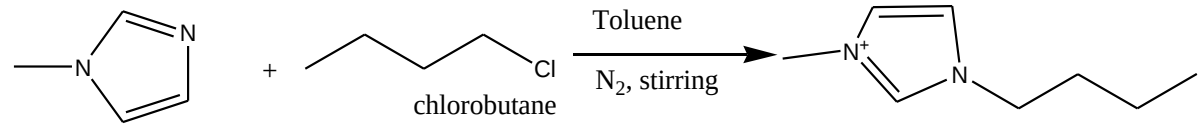
MATERIALS AND METHODS

2.1 Materials

1-Methylimidazole (99%) and 1-chlorobutane (99.5%) were purchased from sigma Aldrich and were distilled over KOH and P_2O_5 respectively, before use. Hexafluorophosphoric acid (*ca.* 65% solution in water), 1-chlorooctane and TEOS are also purchased from sigma Aldrich and was used without purification. Methanol, HCL and toluene were purchased from Himedia.

2.2 Syntheses of ionic liquids and silica ionogels

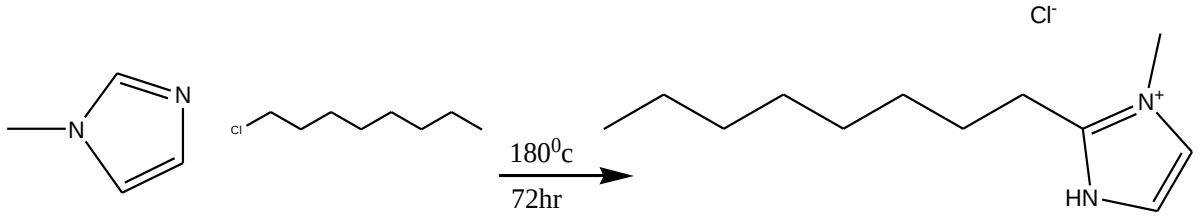
2.3 Preparation of 1-butyl-3-methylimidazolium chloride (bmimcl) ionic liquid



1-methylimidazole

To a 100 ml round bottom flask equipped with reflux condenser, magnetic stirring bar connected with a nitrogen cylinder, 1-methyl imidazole 10 ml (125 mmol) and toluene 12.32 ml (mmol) was added in ice bath. After 5 min. of stirring 1-chlorobutane 14.2 ml was added. Then the solution was heated to reflux at 80 °C for 72 h, yielding a two phase mixture of ionic liquid [BMIMCl] and toluene which were then separated and recrystalized with acetone. ^{1}H-NMR($CdCl_3$, 400MHz): δ(ppm) = 10.52 (s, 1H, NCHN), 7.58 (m, 1H, $CH_3NCHCHN$), 7.43 (m, 1H, $CH_3NCHCHN$), 4.32 (t, 2H, $NCH_3(CH_2)_2CH_3$), 4.09 (s, 3H, NCH_3), 1.82 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.94 (t, 3H, $N(CH_2)_3CH_3$).

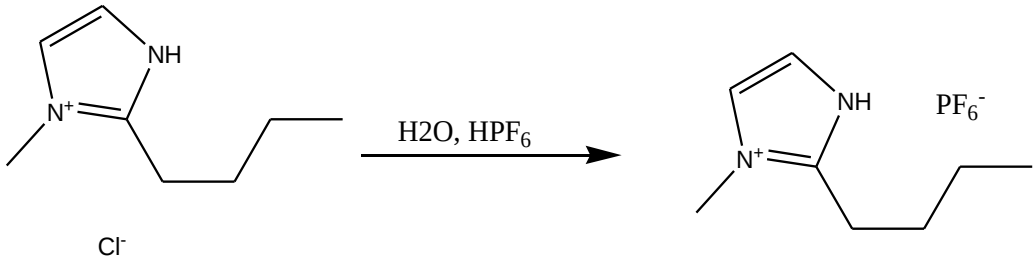
2.4 Preparation of 1-octyl-3-methylimidazolium chloride (omimcl):



1-methylimidazole 1 chlorooctane 1-octyl 3-methyl imidazolium chloride

To a 100 ml round bottom flask equipped with reflux condenser, magnetic stirring bar connected with a nitrogen cylinder, 1-methyl imidazole 10 ml (125 mmol) and toluene 12.6 ml was added in ice bath. After 5 min. of stirring 1-chlorooctane 23.44 ml (138 mmol) was added. The solution was heated to reflux at 125 °C for 72 h, yielding a two phase mixture of [OMIMCl] and toluene. Then the toluene was decanted and the product was recrystalized with acetone. ^{1}H-NMR ($CdCl_3$, 400MHz): δ (ppm) = 10.28 (s, 1H, NCHN), 7.61(t, 1H, NCHCHN) 7.38(t, 1H, NCHCHN), 4.17(t, 2H, NCH2 $(CH2)_6CH_3$), 3.98(s, 3H, NCH3), 0.71(t, 3H, CH3)

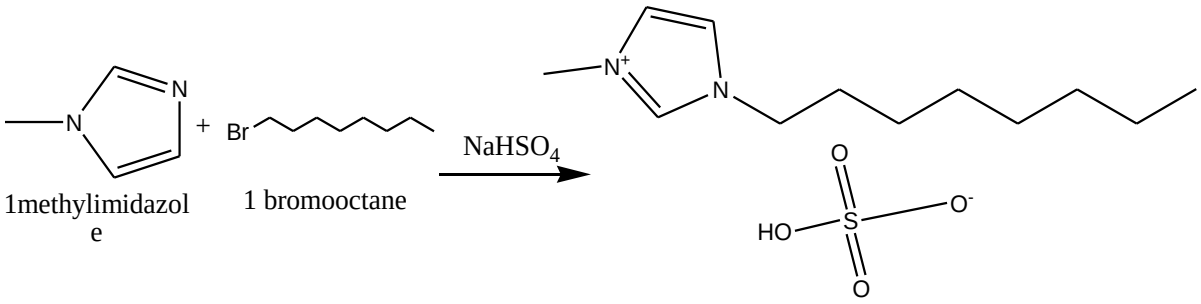
2.5 Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate:



1-butyl 3-methyl imidazolium chloride 1-butyl 3-methylimidazolium hexafluorophosphate

In a typical synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate, BMIMCL (17 mmol) was transferred to round bottom flask followed by the addition of 40 ml of deionised water. An aqueous solution of 65% HPF_6 in a 1.1:1 molar ratio was added slowly to minimise the amount of heat generated. As HPF_6 was added two phases formed, where $BMIMPF_6$ was the bottom phase and the HCl was the upper phase. The upper phase was decanted and the remaining product was washed with water several times. Then the resulting product was dried at 70° C on a vacuum line for 4 h to get the desired product. ^{1}H-NMR($CdCl_3$, 400MHz): δ(ppm) = 8.29 (s, 1H, NCHN), 7.258 (d, 1H, $CH_3NCHCHN$), 7.22 (d, 1H, $CH_3NCHCHN$), 4.05 (m, 2H, $NCH_2(CH_2)_2CH_3$), 3.78 (s, 3H, NCH_3), 1.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.816 (t, 3H, $N(CH_2)_3CH_3$).

2.6 Synthesis of 1-octyl-3-methylimidazolium hydrogen sulphate ($OMIMHSO_4$) using microwave:



1methylimidazole 1 bromooctane 1-octyl-3-methylimidazolium hydrogen sulfate

A typical synthesis involved mixing a 1.05 molar excess of1-chloro-octane (60.9 mmol) to 1-methylimidazole (58.0 mmol). To this mixture $NaHSO_4$ (2.0 g) was added .The mixture was then irradiated in a microwave for 5 min at300 W to a maximum temperature of 110° C. After this time additional $NaHSO_4$ (2.0 g) was added and irradiated again. This procedure was repeated until a molar equivalent of$NaHSO_4$ (7.32 g, 60.9 mmol) had been added. After the final addition, the reaction mixture was irradiated for 12 min at 300 W at 110° C. The product was extracted with CH_2Cl_2 (100 mL) and filtered to remove the salts. The solvent was removed in vacuum and the resultant oil were washed with diethyl ether (2 ×100 mL). The product was then dried in vacuum at80° C to afford the product. ^{1}H-NMR($CDCl_3$,

400MHz): δ(ppm) = 10.65 (s, 1H, NCHN), 7.28(d,1H,NCHCHN) 7.21(t,1H,NCHCHN), 3.71(s,3H,NCH_3)

2.7 Synthesis of mesoporous silica nanoparticles (MSN)

In a typical synthesis of MSN, 1-octyl 3-methylimidazolium chloride (2.74 mmol) was dissolved in 480 ml of 15 mmol NaOH (aq) and the solution was heated to 80^0C, followed by the drop wise addition of tetraethyl orthosilicate (22.4 mmol) and stirred for 2 h to yield the desired product. The ionic liquids used were extracted from the mesoporous by refluxing the as synthesized silica nanoparticles in 200 ml methanolic solution of HCl (520 mmol) for 48h. Finally, centrifugation was done at 2000 rpm to get the desired mesoporous silica nanoparticles.

2.8 Synthesis of silica iono gels by formic acid (solvolytic method):

In a typical synthesis of silica ionogels, the ionic liquid(IL) and formic acid(FA) were stirred at room temperature for 10 min before adding the silica precursor(TEOS) in a molar ratio of 1 TEOS/0.5 IL/7.8 FA. The resulting solution was stirred at room temperature for 10 min. Gel times depend on the IL. The removal of IL was performed by means of Soxhlet extractor with refluxing acetonitrile. (IL used in this synthesis is BMIMCl, OMIMCl and $OMIMHSO_4$)

2.9 Characterization of ionic liquid, silica gel and silica nanoparticles

The materials synthesized in above sections were characterized by nuclear magnetic resonance spectroscopy, Scanning Electron Microscopy, UV-Visible spectroscopy (UV-Vis), Thermo Gravimetric analysis (TGA). To check purity of ionic liquid NMR was taken.

UV-Vis Spectroscopy

UV-Vis Spectra of pure BMIMCl and $BMIMPF_6$ materials were recorded on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900 nm.

Nuclear magnetic resonance spectroscopy

After the synthesis of ILs, they were analyzed by ^{1}H NMTR to check the purity of the samples. NMR was taken on a 400 MH_Z Bruker instrument using $CDCl_3$ as solvent.

Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) was performed using a TA instruments TGA Q5000IR under air flow. TGA Measures changes in weight in relation to changes in temperature.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was taken using JEOL JSM-6480 LV microscope (acceleration voltage 15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder for SEM analysis.

Chapter-3

Results and Discussion

3.1 NMR Study

Fig-1 shows the NMR spectra of 1-butyl-3-methylimidazolium chloride. All the peaks for BMIMCl can be seen in the spectra.

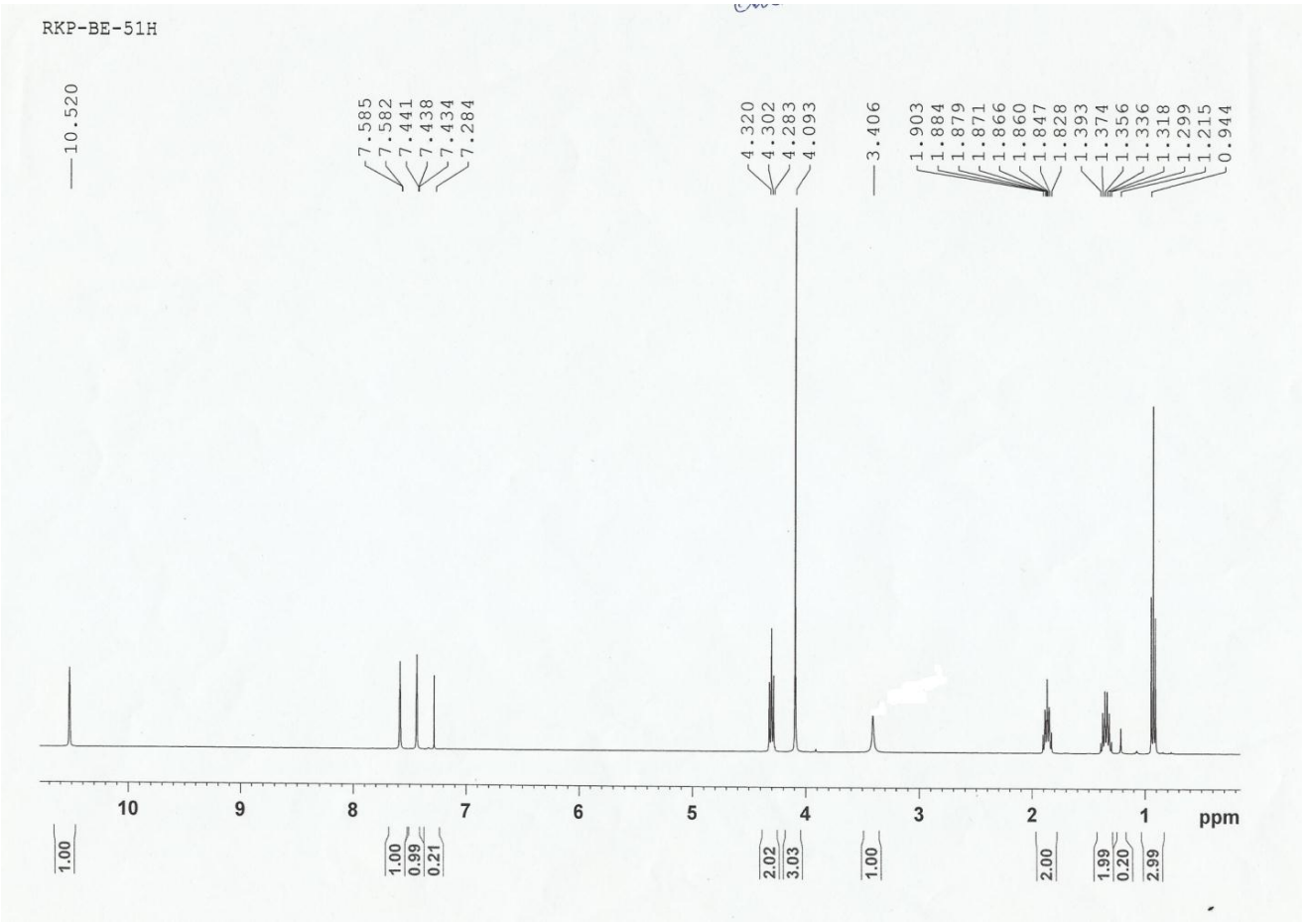


Fig. 1 ^{1} H NMR spectra of BMIMCl.

Fig-2 shows the NMR spectra of 1-octyl-3-methylimidazolium chloride. The absence of peaks other than OMIMCl indicated the purity of the ionic liquid.

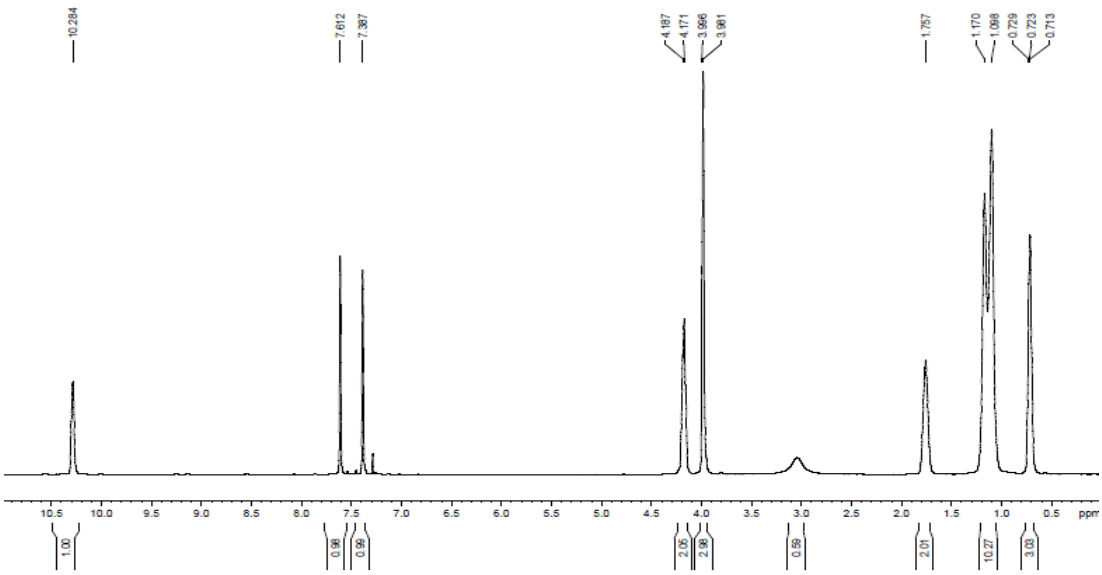


Fig. 2 ^{1} H NMR spectra of OMIMCl

Fig-3 shows the NMR spectra of 1-butyl-3-methylimidazolium hexafluoro phosphate in which all the proton NMR spectrum contained peaks corresponding to the imidazolium cation and indicated no residual reactants.

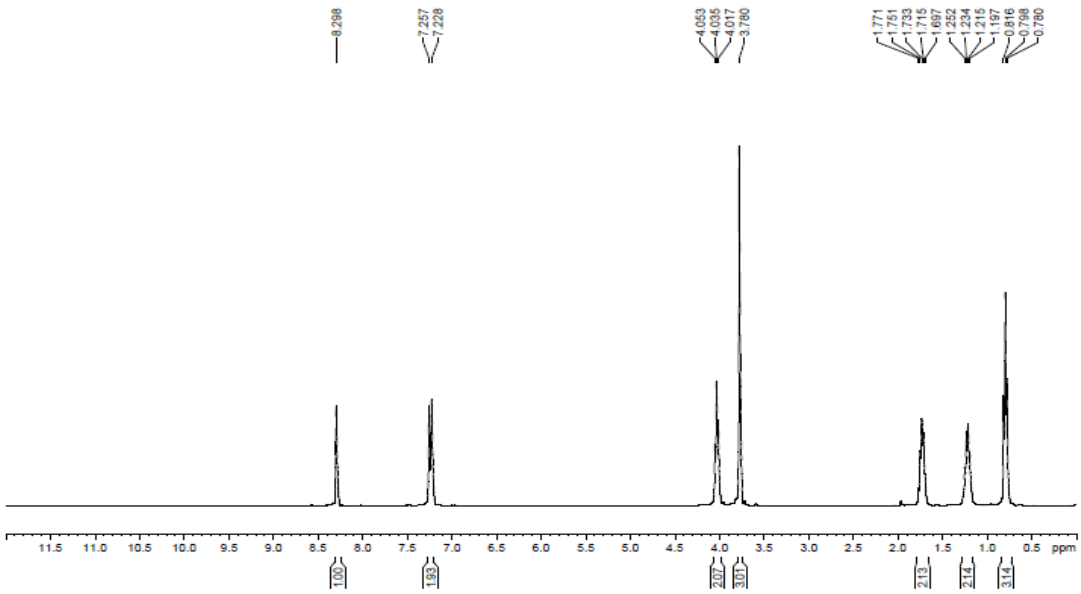


Fig. 3^{1} H NMR spectra of BMIMHPF$_6$.

Fig-4 shows the NMR spectra of 1-octyl-3-methylimidazolium hydrogen sulfate. The spectrum of this ionic liquid exhibits some impurities at δ 0.5-1.5 region.

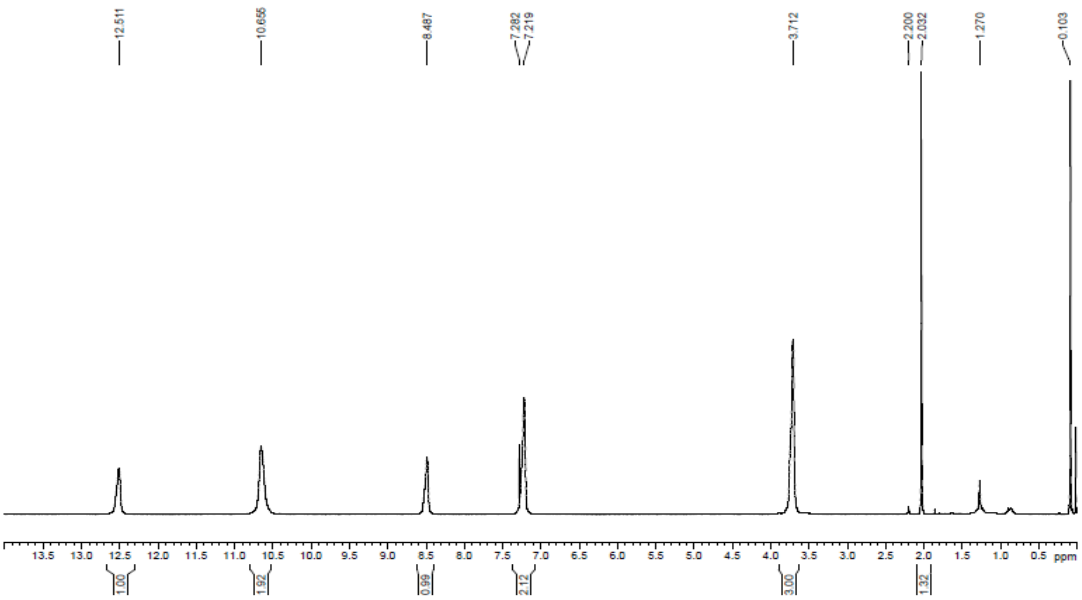


Fig. 4 ^{1} H NMR spectra of $OMIMHSO_4$.

3.2 UV-Vis study:

Ionic liquid is synthesized as mentioned above. The UV-Vis spectra of the pure ionic liquid (1-butyl-3-methylimidazolium chloride) in the scanning range 200-800 nm are shown in Fig. Due to some colour impurities there is a absorption peak at 260 nm.

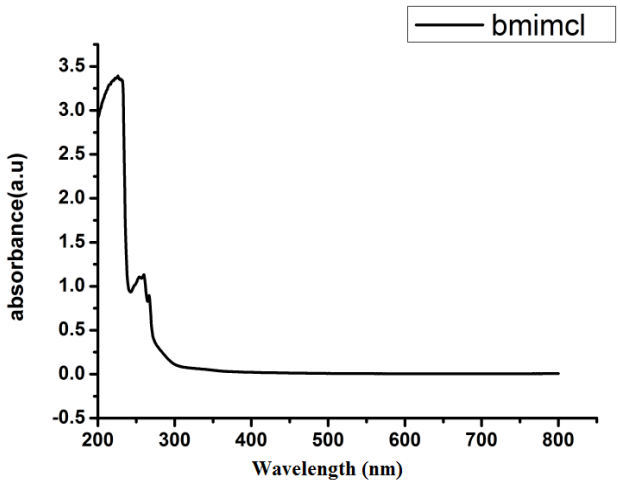


Fig-5 UV-Vis spectra of 1-butyl-3-methylimidazolium chloride

The ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate was prepared as above the procedure. Fig.5shows the UV-Vis spectra of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. No absorption peak below 290 nm has been observed which clearly confirmed the absence of any colored impurities.

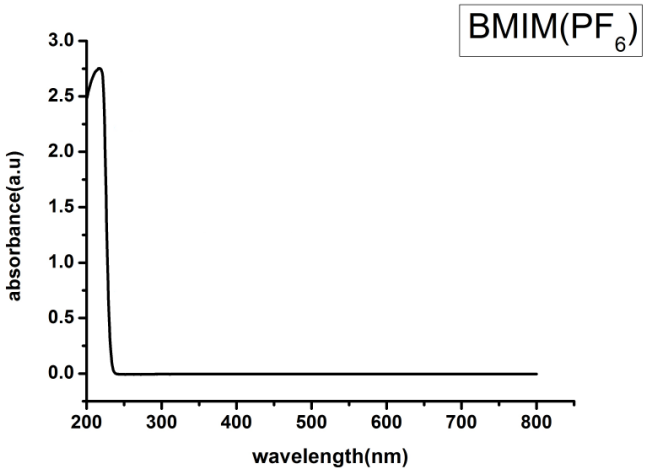


Fig-6 UV-Vis spectra of 1-butyl-3-methylimidazolium hexafluorophosphate.

3.3 Silica Ionogel from BMIMCL and $OMIMHSO_4$:

A highly transparent silica iono gel was obtained. The gel time depends upon the ionic liquids. Silica iono gel from BMIMCl took 3 h for the formation of gel and for $OMIMHSO_4$ the gel time was 4 h.

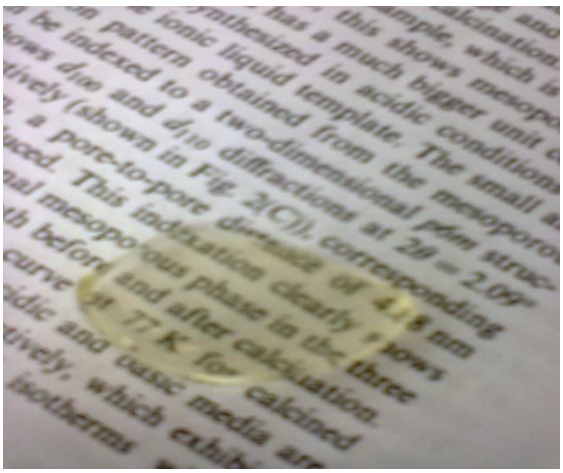


Fig7 Silica ionogel synthesized in BMIMCl .

Fig-8 Silica ionogel synthesized in $OMIMHSO_4$

3.4 TGA Plot

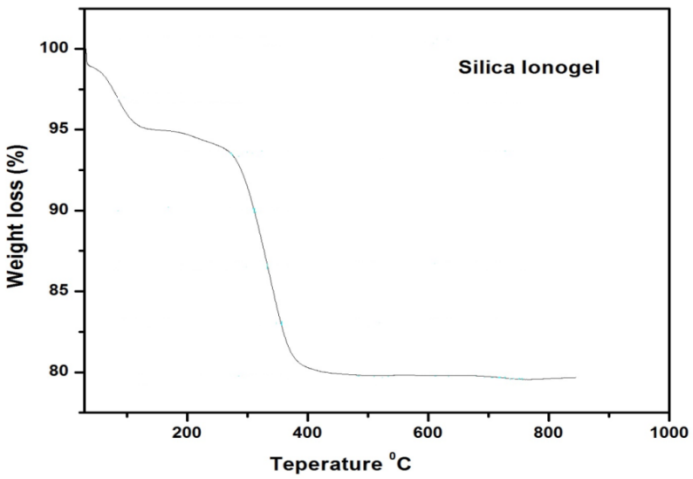


Fig-9 TGA plot of washed gel after extraction of BMIMCl in acetonitrile.

Thermo gravimetric analysis (TGA) was performed using a TA instruments TGA Q5000IR under air flow. Initial samples were run from 25 °C to 600 °C with a heating rate of 5 °C/min to determine the IL present in the samples and the degradation temperature range. As can be seen form the image, most of the ILs was removed after heating at 400 °C which resulted in the formation of porous silica. This substantial IL residue could be of interest for some applications such as catalysis. After the removal of ILs, porous silica powder was obtained.

3.5 SEM study:

The scanning electron micrographs of silica ionogels materials were prepared by solvolytic method.SEM micrographs were taken to determine the maximum, minimum and mean diameter size. The morphology of the particles is shown in the SEM micrographs presented in Figure 5.The materials particles have the appearance of spherical objects, spherical-like objects, which seemed to be a junction of various circular and perforated objects with a variable length and diameter.

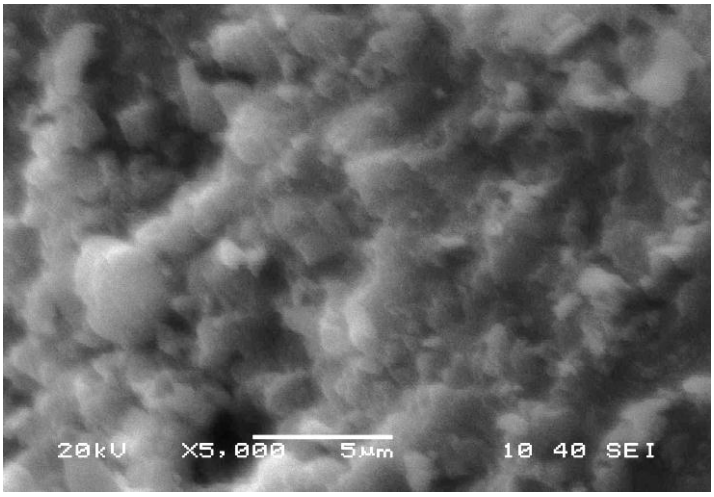


Fig. 10 SEM image of washed gel after extraction of BMIMCl in acetonitrile

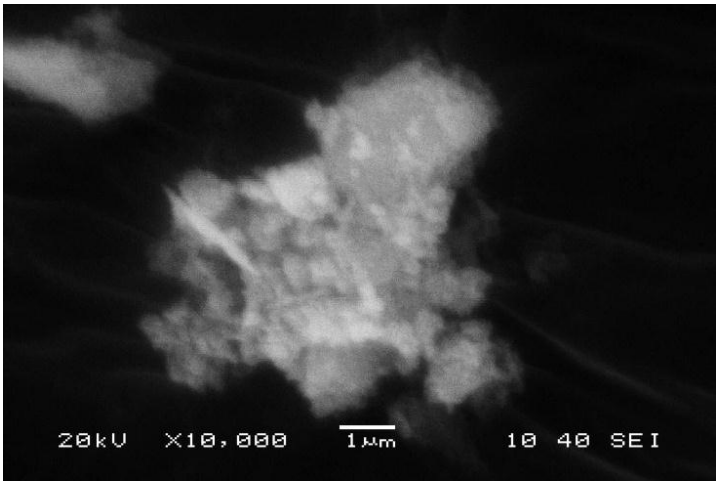


Fig.11 SEM image of Silica nanoparticles synthesized in OMIMCl

In scanning electron microscope the morphology of the synthesized silica nanoparticle was investigated in terms of dimension, shape and aggregation. The scanning electron microscope of silica nanoparticles shows in fig. 6.In micrographs the particle has round shape and uniform in arrangement. They are fairly monodispersed in nature.

Chapter-4

CONCLUSION

The formic acid solvolytic method was employed to synthesize silica iono gels. A highly transparent silica gel was formed which was washed to remove ionic liquids by Soxhlet extractor

using acetonitrile. About 20% of ionic liquid was remaining in the silica iono gel which could be of interest for some application such as catalysis. . The SEM results showed that the formation of silica ionogels. Silica nanoparticles are synthesized by using ionic liquids and characterized by SEM. The ionic liquids in case of silica nanoparticles were extracted by refluxing with methanolic solution of HCl and remaining ionic liquids were removed by calcinations at 500 °C.

References

[1] Mazumder, S.; Sen, D.; Sastry, P U M.; Chitra, R.; Sequeira, A.; and Chandrasekaran, K S; J. Phys. Condens. Matter 10, **1998,** 9969

[2] Sen,D.; Patra, K. A.; Mazumder, S; and Ramanathan, S.; 361,

2003, 270

[3] Sen,D.; Patra, K. A.; Mazumder, S; and Ramanathan, S.; J. 340, **2002,** 236

[4] Sen, D.; Mahata, T.; Patra, K.A.; Mazumder,S.; and Sharma,P. B.; J. Alloys and Compounds,364, **2004,** 304

[5] Ribot,J.C .; Guerrero-Sanchez,C.; Hoogenboom.R.; and Schubert,U.S.; J. Mater. Chem., **2010**, 8279.

[6] Vioux, A.; Viau, L.; Volland, S and J. Le Bideau, C. R. Chim.13, **2010**, 242.

[7] BideauLe.Jean,;Viau, Lydie and Vioux, André.; Chem. Soc. Rev., 40,**2011**, 907.

[8] Handy, S. T.; Curr. Org. Chem., 9,**2005**, 959.

[9] Weingaertner, H. Angew. Chem. Int. Ed., 47,**2008**, 654.

[10] Ze Yu, Nick Vlachopoulos, Mikhail Gorlov and Lars Kloo, Dalton Trans., 40,**2011,** 10289.

[11] Nathalie Cheminet, ThibautJarrosson, Jean-Pierre Lère-Porte, Françoise Serein-Spirau, LuizCury, Joel Moreau, LydieViau and André Vioux, J. Mater. Chem.21,,**2011**, 13588.

[12] SrivastavaSachin K.; Gupta Banshi D. Sens. Actuators, B,156,**2011**,559.

[13] Schmidt. C.; T. Gluck and Schmidt-Naake, G.; Chem. Eng. Technol. 31,**2008**, 13.

[14] Ueki, T.; and M. Watanabe.; Macromolecules,41,**2008**, 3739.

[15] Karakassides, M.A.; Bourlinos, A.; Petridis, D.; Coche-Guerente, L.; Labbe, P. 10, **2000**, 403–408.

[16] Naik, S.P.; Chiang, A.S.T.; Thompson, R.W. **2003**, 7006

[17] Yang, X.Y.; Zhang, S.B.; Qiu, Z.M.; Tian, G.; Feng, Y.F.; Xiao, 108, **2004**, 4696–4700.

[18] Song, K.; Guan, J.; Wang, Z.; Xu, C.; Kan, Q..255, **2009**, 5843–5846.

[19] AlOthman, Z.A.; Apblett, A.W. J.155, **2009**, 916.

[20] AlOthman, Z.A.; Apblett, A.W. 6, **2009**, 2331.

[21] AlOthman, Z.A.; Apblett, A.W.256, **2010**, 3573–3580.

[22] Davis, M.E.; Lobo, R.F. Chem. Mater. 4, **1992**, 756–768.

[23] Mitchell, P.C.H..6, **1991**, 308.

[24] Ozin, G.A.. Adv. Mater.10, **1992**, 612–649.

[25] Jones, R.H.; Thomas, J.M.; Chen, J.; Xu, R.; Huo, Q.; Li, S.; Ma, Z.; Chippindale, A.M. 102, **1993**, 204–208.

[26] Yanagisawa, T.; Schimizu, T.; Kiroda, K.; Kato, C. 63, **1990**, 988–992.

[27] Beck, J.S.; Calabro, D.C.; McCullen, S.B.; Pelrine, B.P.; Schmitt, K.D.; Vartuli, J.C. 722, **1992**.

[28] Zhao, D.J.; Sun, Q.L.; Stucky, G.D. Mater. 12, **2000**, 275–279.

[29] Colilla, M.; Balas, F.; Manzano, M.; Vallet-Regí, M..19, **2007**, 3099–3101.

[30] Puputti, J.; Jin, H.; Rosenholm, J.; Jiang, H.; Lindén, M. 126, **2009**, 272–275.

[31] Rahmat, N.; Abdullah, A.Z.; Mohamed, A.R. 7, **2010**, 1579–1586.

[32] Shields, J.E.; Lowell, S.; Thomas, M.A.; Thommes, M. **2004**, 43.

[33] Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Baltork, I.M.; Ghani, K. 10, **2009**, 853.

[34]Earle, M. J.; McCormac, P. B.; Seddon, K. R. J. Chem. Soc., Chem. Commun. **1998**, 2245

[35]Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. J. Mater. Chem.8, **1998**, 2627

[36]Wilkes, J. S.; Zaworotko, M. J. J. Chem. Soc., Chem. Commun.**1992**, 965.

[37]Dong Q, Muzny C D, Kazakov A, Diky V, Magee J W,Widegren J A, Chirico R D, Marsk K N &Frenkel M, JChemEng Data, 52 ,**2007,** 1151.

[38]Baker, A.G.; Pandey, S.; Pandey, S.; Baker, N. S.; Analyst 129 ,**2004**, 890.

[39]Baker, A.G.; Baker, N. S.; McCleskey,T.M.; Chem. Commun. **2003**, 2932.

[40]Baker,N.S.; McCleskey, T.M.; Pandey, S.; Baker, A.G.; Chem. Commun. **2004** 940.

[41]Fletcher, A.K.; Pandey, S.; Storey, I.K.; Hendricks, E. A.; Pandey, S.; Anal. Chim.Acta453 ,**2002** 89.

[42]Baker, A.G.; Baker, N.S.; Aust. J. Chem. 58 ,**2005** 174.